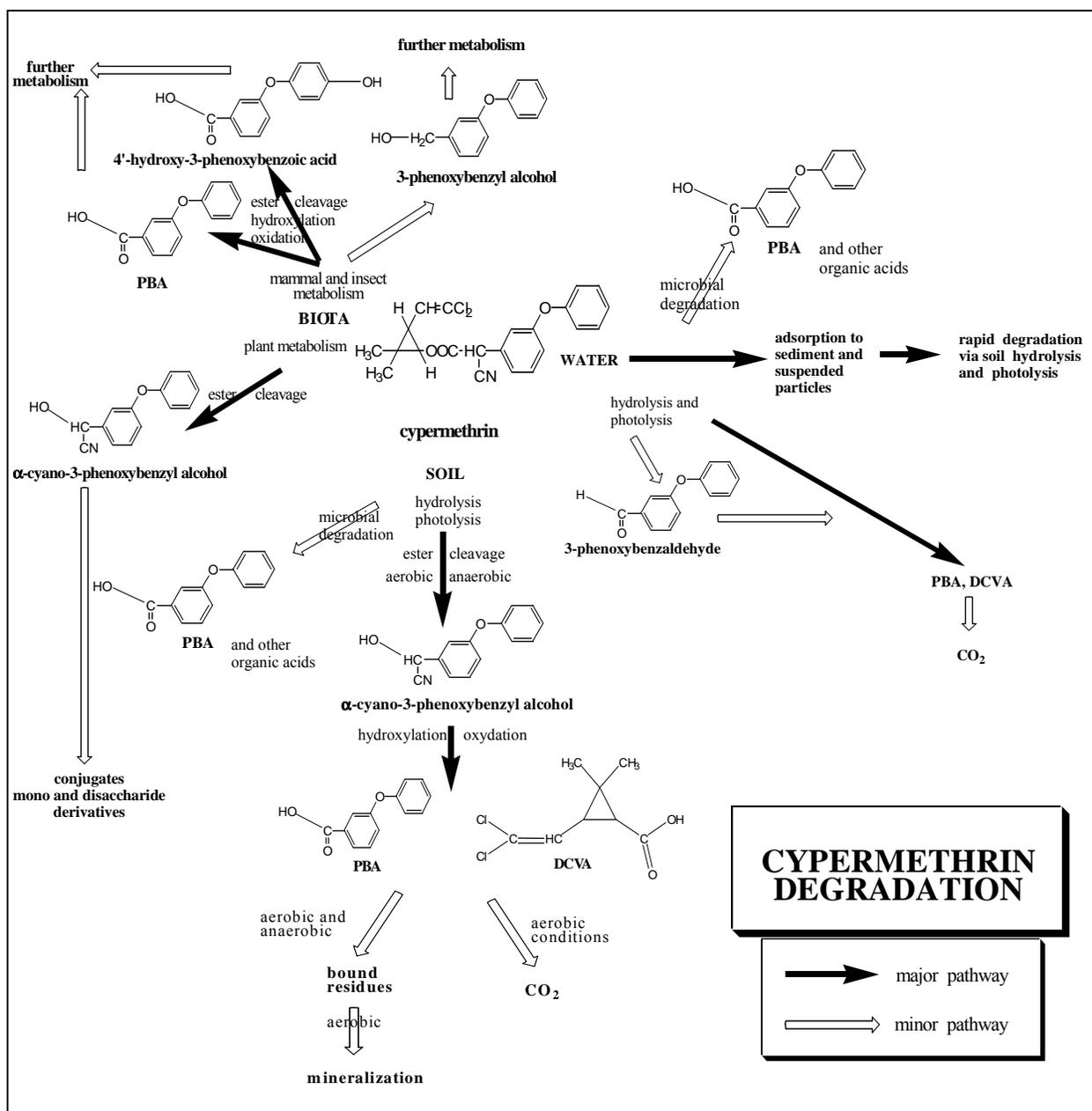# ENVIRONMENTAL FATE OF CYPERMETHRIN

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This document reviews the environmental fate of cypermethrin [(±)-∝-Cyano-(3-phenoxyphenyl)methyl (±)-*cis/trans*-3-(2,2-dichlorovinyl)-2,2 dimethylcyclopropane carboxylate]. Cypermethrin is a synthetic, pyrethroid insecticide that is available in several formulations as an emulsifiable concentrate or wettable powder.

CYPERMETHRIN DEGRADATION

Cypermethrin[a]

Molecular formula[b]	$C_{22}H_{19}O_3NCl_2$
Molecular weight[b]	416.3
Water solubility (at 20^0 C)	4 ppb
Vapor pressure (at 20^0 C)	1.3×10^{-9} mmHg
Henry's Law Constant (average of 3 pH's at 20^0C)	2.5×10^{-7} atm-m^3/mol
Hydrolysis half-life (at env. expected temps. and pH values)[b]	>50 days
Octanol-water coefficient (K_{ow})	3.98×10^6
Soil adsorption coefficient (K_{oc}) (avg. of data for five soil types)[c]	6.1×10^4 mL/g or cm^3/g
Field dissipation half-life[b]	4-12 days
Aerobic half-life[c]	6-20 days
Anaerobic half-life[c]	<14 days

a- Data from Kollman and Segawa (1995)
b- Data from EPA's Pesticide Fact Sheet Database (1992)
c- Data from USDA Agricultural Research Service (1995)

Toxicity[a]

Rat (oral, acute)	LD_{50} 247 mg/kg (males)
	LD_{50} 309 mg/kg (females)
Rabbit (acute, dermal)	LD_{50} > 2460 mg/kg
Mallard Duck (oral, acute)[b]	LD_{50} > 10,000 mg/kg
Chickens (acute, oral)[b]	LD_{50} > 2000 mg/kg
Mallard Duck and Bobwhite Quail (oral)	LC_{50} >20,000 ppm
Brown trout (96 hrs)[b]	LC_{50} 2.0-2.8 ppb
Rainbow Trout (96 hrs)	LC_{50} 0.82 ppb
Bluegill Sunfish (96 hrs)	LC_{50} 1.78 ppm
Daphnia magna	LC_{50} 0.26 ppb
Honeybee[c]	LD_{50} 0.025 µg/bee

a- Data from EPA's Pesticide Fact Sheet Database (1992)
b- Data from The Agrochemicals Handbook, Third Edition (1991)
c- Data from J. Delabie *et al.*, 1985

General Characteristics and Mode of Action

Cypermethrin is a synthetic, pyrethroid insecticide that has high insecticidal activity, low avian and mammalian toxicity, and adequate stability in air and light (Kaufman *et al*.,1981, and U.S.D.A., 1995). It is used to control many pests including lepidopterous pests of cotton, fruit, and vegetable crops and is available as an emulsifiable concentrate or wettable powder. According to the label for Ammo® 2.5 EC insecticide, which contains 2.5 pounds of cypermethrin per gallon, the product should not be applied directly to water or to areas where surface water is present. Also, cypermethrin should not be applied when wind may cause drift beyond the intended treatment area. Due to its extreme toxicity to fish and aquatic organisms, Ammo® 2.5 EC is registered as a "restricted use pesticide", and is for sale to, and to be used only by, Certified Applicators.

In vertebrates and invertebrates, cypermethrin acts mainly on the nervous system**.** Cypermethrin is both a stomach poison and a contact insecticide (Jin and Webster, 1998). In the peripheral nervous system of the frog**,** its primary action is to induce noticeably repetitive activity and produce trains of nerve impulses as a result of altering ion permeability of nerve membranes (Vijverberg and van den Bercken, 1990; and Siegfried, 1993). These long-lasting trains can cause hundreds to thousands of repetitive nerve impulses in the sense organs. This repetitive activity is induced by pyrethroid damage to the voltage-dependent sodium channel, causing sodium channels to stay open much longer than normal. (Vijverberg and van den Bercken, 1990).

Cypermethrin has been shown to inhibit ATPase enzymes involved in movement of ions against a concentration gradient which are regulated by active transport. This action is especially critical to fish and aquatic insects where ATPase enzymes provide the energy necessary to active transport, and are very important at sites of oxygen exchange. ATPase inhibition and disruption of active transport, possibly affect ion movement and the ability to maintain ion balance, and disrupt respiratory surfaces, indicating that cypermethrin is inherently more toxic to aquatic organisms (Siegfried, 1993).

Physical Chemical Properties and Environmental Fate of Cypermethrin

Air: Cypermethrin has a very low vapor pressure and is not readily volatilized into the atmosphere. A low Henry's Law Constant (H) , 2.5×10^{-7} atm-m^3/mol at 20^{0}C, indicates that cypermethrin has almost no tendency to volatilize from an aqueous solution. According to Lyman *et al*. (1982), if the H is less than about 3×10^{-7} atm-m^3/mol, as it is for cypermethrin, the substance is less volatile than water and can be considered virtually nonvolatile. Experimental results indicate that there is practically no movement of cypermethrin from contaminated soils to the surrounding air (Bacci *et al*., 1987), unless bound to air-borne particulates. Aside from drift that may occur with spray applications, cypermethrin is not expected to be found in air.

Soil: Cypermethrin occurs as a mixture of both the *cis* and *trans* isomers. The *cis/trans* ratio in technical grade cypermethrin is 1:1 (Kidd and James, 1991). The *cis* isomers are more active than *trans* by a factor of two. No significant difference was observed between the photodegradation rates of the two isomers in soil, although the *trans*-isomer was hydrolyzed 1.2-1.7 times faster (Takahashi *et al*., 1985). Hydrolysis and photolysis play major roles in the degradation of

cypermethrin in soil. Hydrolysis of the ester linkage is the principal degradation route and leads to the formation of 3-phenoxybenzoic acid (PBA) and cyclopropanecarboxylic acid derivatives (Sakata *et al*., 1986), principally, 3-(2,2-dichlorovinyl)-2,2-dimethyl cyclopropanecarboxylic acid (DCVA) (Kaufman *et al*., 1981). Cypermethrin also photodegrades rapidly on soil surfaces to many byproducts, with half-lives of 8-16 days (Walker and Keith, 1992). Many photoreactions are involved in photodegradation and the photodegradation rates are closely correlated with the organic matter content of the soil (Takahashi *et al*.,1985). As with hydrolysis, the principal photoproducts of cypermethrin are PBA and DCVA with >15% recovery of each after 32 days of irradiation (Hall *et al*.,1981). Under aerobic conditions, these metabolites may undergo further breakdown to CO_2 at a much slower rate (Kaufman *et al*.,1981; Bacci *et al*., 1987). The persistence of the metabolites is unknown (Walker and Keith, 1992).

Cypermethrin displays low water solubility, hence is hydrophobic. Cypermethrin is a non-polar pesticide and readily adsorbed onto the soil surface and bound there. According to Kaufman *et al*. (1981), very little cypermethrin insecticide would move through the soil profile, although all of the degradation products are more mobile than the parent product. The degradates PBA and DCVA are organic acids which are often mobile in soil. The carbon content of the soil greatly affects the amount of chemical that is adsorbed. Cypermethrin was found to have an average K_{oc} of 6.1×10^4 cm^3/g for five different soil types (USDA ARS, 1995) indicating that cypermethrin is immobile in soil. The major metabolites, on the other hand, are very polar, and move readily through the soil. These organic acids varied in their mobility from intermediate (in silty clay or loamy sand) to mobile (in silty clay loam) (Kaufman *et al*., 1981). For PBA and DCVA, a low pH suppressed ionization, thus increasing adsorption and decreasing mobility in more acidic soils. Therefore, these metabolites would be fairly mobile in neutral to alkaline soils (Kaufman *et al*., 1981).

Microbes play a significant role in the degradation of cypermethrin. Cypermethrin degrades more slowly under anaerobic and waterlogged conditions (Walker and Keith, 1992). The anaerobic half-life reported at <14 days is similar to the half-life in aerobic soils ranging from 6-20 days (USDA, 1995), but the major metabolite, PBA, does not continue to break down anaerobically (Leahey, 1985). The chemical also degrades more slowly in sterilized versus natural soils which illustrates the importance of microorganisms (Chapman *et al*., 1981). In sterile aerobic soils, the half-life was 20 to 25 weeks (Walker and Keith, 1992).

Cypermethrin is relatively non-persistent in soils with the typical half-life in sandy soils of 2-4 weeks (Chapman and Harris, 1981). Increased cypermethrin persistence was observed in soil with high organic matter, high clay content, reduced microbial activity and anaerobic conditions (Chapman *et al*.,1981).

Water: The water solubility of cypermethrin is very low, 4 ppb at 20^0C (Kollman and Segawa,1995). Cypermethrin is extremely hydrophobic and will quickly move from an aqueous solution to suspended particulates (Fitzpatrick, 1982). Thus, relatively small amounts of suspended matter in natural bodies of water may remove a significant amount of cypermethrin from the aqueous phase. Soils and sediment are the main environmental reservoirs for cypermethrin (Bacci *et al*.,1987).

Cypermethrin hydrolyzes slowly in water at pH 7 and below, with hydrolysis being more rapid at pH 9. Under normal environmental temperatures and pH, cypermethrin is stable to hydrolysis with a half-life of >50 days. It is also stable to photolysis with a half-life of >100 days. In sterile solution in sunlight, cypermethrin photodegrades slowly, with <10% lost in 32 days (Walker and Keith, 1992). In darkness, cypermethrin was fairly stable with 88.7 and 95.6% recovery after 10 days in river water and distilled water, respectively (Takahashi *et al*., 1985). Kidd and James, (1991), reported that in river water, rapid degradation occurred with a half-life of about 5 days, which is three to four times faster than degradation in distilled water. This suggests indirect photolysis involving naturally occurring substances that result in enhanced photodegradation. When photodegradation of cypermethrin occurs, the major photoproducts produced are DCVA and PBA, with the a small amount of 3-phenoxybenzaldehyde as a minor photoproduct (Takahashi *et al*., 1985).

According to Agnihorti *et al.* (1986), the reduction in cypermethrin aqueous concentrate was rapid, with about 95% lost within 24 hours after application to water and sediment contained in open trenches. In that study the reduction in concentration was primarily due to rapid sorption to sediment and suspended particles and not degradation. The partition coefficient of cypermethrin is very high (K_{ow}=3.98x10^6), consequently it binds strongly onto organic matter (Crossland, 1982). Because of its strong affinity for soil, cypermethrin may be carried away to nearby water bodies in suspended sediment by rain and irrigation. Yet, once the pesticide is adsorbed to soil particles, bioavailability is reduced, diminishing the toxicological risk to aquatic animals (Agnihorti *et al.*, 1986). In pond experiments, fish have survived in pond water that contained apparently lethal concentrations of cypermethrin (5 ppb) because the chemical was sorbed onto suspended solids (Crossland, 1982).

Biota: Synthetic pyrethroids are extremely effective against insects, but are relatively safe to mammals and birds. One potential problem of pyrethroids is their extreme toxicity to aquatic organisms, where often <1 µg/L will produce toxic effects (Siegfried, 1993). According to Bacci *et al*., 1987, high lipoaffinity and very low water solubility of cypermethrin suggest a strong bioconcentration potential in aquatic organisms when present in a contaminated aquatic environment. Siegfried (1993), suggests that aquatic insects show higher susceptibility to cypermethrin than terrestrial insects because of lower levels of exposure to lipophilic compounds in an aquatic environment which leads to lower potential to detoxify lipophilic xenobiotics such as insecticides.

According to Muir *et al*., 1985, in laboratory and field studies, cypermethrin concentrations decreased rapidly by adsorbing to sediment, suspended particulates and plants. Also, there was rapid photochemical and microbial transformation. In these experiments, cypermethrin degraded much more slowly in sediment than in water above sediment. This suggested that sediment may act as a reservoir to add intact chemical to the water for a long period of time. The amount of chemical that will partition from sediment to water varies among types of sediment. In the study conducted by Muir *et al*. (1985), 55% of *trans*-cypermethrin moved to the water above sand, and only 4% moved to the water above silt or clay in a 24 hour period. Larvae (*Chironomus tentans*) that were kept in direct contact with sediment had bioconcentration factors (BCFs) up to two times greater at high concentration exposure (174 ng/g and 640 ng/g for *cis* and *trans* isomers, respectively) than those held in water above sediment. All larvae held in sand or water above

sand had higher BCFs than those held in silt or clay systems. The BCF of cypermethrin in rainbow trout (180-438) is far lower than expected when considering its K_{ow} value. One possible explanation is the inefficient uptake of hydrophobic chemicals via the gills. Cypermethrin's hydrophobicity and strong adsorption ability affect it's bioavailability to fish (Muir *et al*., 1994). Therefore, in systems with more dissolved organic carbon (DOC) and suspended particulates Cypermethrin displays lower bioavailability to aquatic organisms and fish than systems that are relatively particulate-free.

Most of the studies conducted on the dissipation of cypermethrin in biota determine the metabolic pathways. Because pyrethroid treated crops may be eaten by livestock, metabolism in such animals has been studied, but not as extensively as in laboratory animals. In one study by Chen *et al*., (1997), holstein dairy cows were fitted with eartags containing cypermethrin and/or dosed orally with cypermethrin for 28 days to determine residues in milk and tissues. The results from that study showed that cypermethrin residues did not exceed 19 ppb in the milk samples when cows were given a 5 ppm daily dose, the expected maximum intake level, and the acid metabolites were non detectable. Also, all tissue samples were at or below the detection limit for cypermethrin and its metabolites, except for fat samples which had up to 125 ppb of cypermethrin. It was reported that most of the chemical was eliminated in approximately equal proportions (45%) in the urine and feces. The study showed that daily ingestion of cypermethrin as high as 50 ppm in the diet for 28 days had no effects on lactating dairy cows.

Cypermethrin is readily excreted by rats and mice, leaving low residues after 8 days (Leahey, 1985). Even though cypermethrin has a high lipoaffinity, it is not significantly stored in the fatty tissues and is excreted primarily intact.   The metabolism of cypermethrin involves a wide range of pathways, with the primary pathway being cleavage of the ester bond. Cypermethrin is primarily a mixture of *cis* and *trans* isomers, with a *cis* configuration greatly reducing the cleavage rate. Therefore, *cis*-cypermethrin is more metabolically stable, but is still efficiently metabolized for rapid excretion. The major metabolites formed are PBA and 4'-hydroxy-3-phenoxybenzoic acid. Although there have been no detailed reports on the metabolism of cypermethrin by insects, the data suggests that the pathways are similar to those in mammals. Leahey (1985) has suggested that cypermethrin is much more toxic to insects than mammals because the insect metabolism rate is much slower.

In plants, the metabolic cypermethrin degradation pathways have been studied in lettuce and cabbage plants. The primary metabolic reaction is ester cleavage which produces α-cyano-3-phenoxybenzyl alcohol. Hydroxylation also occurs in various positions, but is a fairly minor pathway. Studies were conducted under field and greenhouse conditions. Degradation occurred more rapidly under field conditions with the greenhouse half-life reported to be approximately 8 days (Leahey, 1985). Furuzawa *et al*. (1981) reported different half lives for *cis*- and *trans*-cypermethrin isomers in cabbage. The initial degradation half-lives on and in cabbage leaves were 4-5 and 7-8 days for *trans* and *cis* isomers, respectively. Therefore, *cis* isomers remain active longer and degrade more slowly than *trans* isomers.

Cypermethrin has also been used to control the elm bark beetle and, according to Jin and Webster (1998), acts more rapidly than chlorpyrifos. Cypermethrin was applied at the basal 1m of the trunks of elm trees. Elm bark, cambium and wood tissue were collected separately to determine

its ability to penetrate, and separate bark samples were taken to determine cypermethrin's persistence. The experimental results indicated that cypermethrin does not penetrate the bark and yet it is still 100% effective in killing bark beetles after 60 days from the application (Jin and Webster, 1998).

Conclusion

Cypermethrin is a synthetic, pyrethroid insecticide that is extremely effective against a wide range of insect pests. The insecticide is both a stomach poison and a contact poison that effects the nervous system of vertebrates and invertebrates, by affecting voltage-dependent sodium channels and inhibiting ATPase enzymes. Cypermethrin is relatively safe to mammals and birds, but is extremely toxic to fish and aquatic organisms, and should not be applied on or near water, or when drift is a possibility.

Because cypermethrin has a low Henry's Law Constant, except for some minor spray drift, it is not expected to be found in air. In soil and water, the major metabolites are PBA and DCVA via hydrolysis and photolysis, with the impurity 3-phenoxybenzaldehyde as a minor byproduct in water. Under aerobic conditions, the metabolites may breakdown further to produce CO_2. The principal degradation route for cypermethrin in soil is hydrolysis of the ester linkage, leading to PBA, DCVA, and eventually CO_2. The persistence of the metabolites is unknown. Cypermethrin is fairly immobile in soil due to its strong affinity to bind to the organic matter. The metabolites, however, vary in their mobility from intermediate to mobile. Other factors effecting the degradation of cypermethrin in soils are pH and microbes. Higher pH increases adsorption, and cypermethrin degrades more slowly in sterile soils.

In water, cypermethrin is relatively stable to hydrolysis and photolysis with the half-lives being >50 and >100 days, respectively. Cypermethrin hydrolyzes and photolyzes more quickly in a basic environment, where the chemical degraded much faster in river water versus distilled water. This suggests that naturally occurring substances enhance the breakdown of cypermethrin, and because of its high affinity for organic matter, cypermethrin readily adsorbs to suspended matter in natural waters.

In mammals and birds, cypermethrin is relatively non-toxic. Studies have shown that, when ingested, laboratory rats and dairy cattle rapidly excrete cypermethrin, posing a low toxicological threat to them. For aquatic organisms and fish, there is a much higher toxicological risk. Because of its high lipoaffinity and low solubility, cypermethrin has a strong potential to bioaccummulate in aquatic animals. However, as described above, in natural waters even small amounts of sediment will adsorb a significant amount of cypermethrin, reducing bioavailability and mitigating bioconcentration in aquatic animals.

When applied topically to cabbage and lettuce plants, cypermethrin is rapidly metabolized to α-cyano-3-phenoxybenzyl alcohol. This type of application is not toxic to the plants, but is toxic to the insects which feed on them. Eventually, cypermethrin will metabolize to mono and disaccharide derivatives. When applied to the bark of elm trees, cypermethrin is much more persistent, maintaining the ability to control bark beetles after 60 days.   The bark, however, appears to be impenetrable to the cypermethrin, yielding undetectable levels in the cambium and

wood tissue layers.

Soil and sediment are the main environmental reservoirs for cypermethrin, where nearly all of the compound ends up. Soil is also the compartment with the highest degradative potential for this chemical, especially those soils with high microbial activity. Sorption to soil and sediment has the net effect of reducing mobility and bioavailability of cypermethrin to sensitive species.

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